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KINETIC STUDIES OF THE COMPLEXATION OF MONOVALENT SODIUM, POTAS--ETC(U)

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Contract N00014-75-C-0796

Task No. NR-051-556

TECHNICAL REPORT, NO. 9

KINETIC STUDIES OF THE COMPLEXATION OF MONOVALENT SODIUM, POTASSIUM,
RUBIDIUM, THALLIUM AND SILVER CATIONS BY AQUEOUS 15-CROWN-5,

by

Licesio J. Rodriguez, Gerard W. Liesegang, Robert D. White,
Michael M. Farrow, Neil Purdie, and Edward M. Eyring

Prepared for Publication in the
Journal of the American Chemical Society

University of Utah
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Salt Lake City, Utah 84112

4 Oct 1976

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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER 9	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) KINETIC STUDIES OF THE COMPLEXATION OF MONOVALENT SODIUM, POTASSIUM, RUBIDIUM, THALLIUM AND SILVER CATIONS BY AQUEOUS 15-CROWN-5		5. TYPE OF REPORT & PERIOD COVERED Technical Report Interim
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Licesio J. Rodriguez, Gerard W. Liesegang, Robert D. White(Univ. of Idaho), Michael M. Farrow, Neil Purdie(Oklahoma State Univ.) and Edward M. Eyring		8. CONTRACT OR GRANT NUMBER(s) N00014-75-C-0796
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Chemistry, University of Utah Salt Lake City, Utah 84112		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS Task No. NR 051-556
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Arlington, Virginia 22217		12. REPORT DATE October 4, 1976
		13. NUMBER OF PAGES 30
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) conformational equilibrium silver(I) 15-crown-5 ultrasonic absorption kinetic studies macrocyclic polyethers alkali metal cations megahertz frequencies thallium(I) aqueous solutions		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) → A kinetic study of the rapid conformation equilibrium of aqueous 15-crown-5 (1,4,7,10,13-pentaoxacyclopentadecane) and of its complexation of monovalent sodium, potassium, rubidium, thallium and silver cations at 25 ^{degree} in aqueous solution has been carried out by ultrasonic absorption in the 15 to 205 MHz →		

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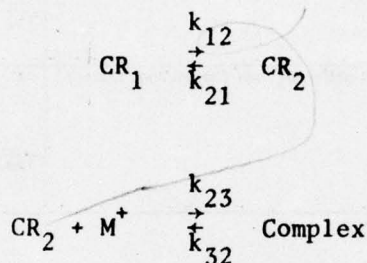
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frequency range.

A concentration independent absorption with a maximum at 22.9 ± 0.5 MHz detected in aqueous solutions of 15-crown-5 with no cations added has been attributed to a conformational rearrangement of the crown ether. The kinetics of the complexation of the polyether with sodium, potassium, rubidium, silver and thallium(I) ions were then investigated at various polyether and metal concentrations with concentration dependent relaxations occurring between 20 and 50 MHz. These data, together with the conformational rearrangement data, were analyzed in terms of a two step mechanism with *



in which CR_2 denotes the conformation of the ether which participates in the complexation reaction.

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* $CR(1)$ rearranging to $CR(2)$
and $CR(2) + M^+$ rearranging
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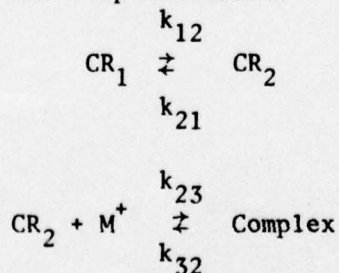
KINETIC STUDIES OF THE COMPLEXATION OF MONOVALENT SODIUM, POTASSIUM,
RUBIDIUM, THALLIUM AND SILVER CATIONS BY AQUEOUS 15-CROWN-5

Licesio J. Rodriguez,^{1a} Gerard W. Liesegang,^{1b} Robert D. White,^{1c}
Michael M. Farrow,^{1b} Neil Purdie,^{1d} and Edward M. Eyring.^{*1b} Contribution from
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Abstract

A kinetic study of the rapid conformational equilibrium of aqueous 15-crown-5 (1,4,7,10,13-pentaoxacyclopentadecane) and of its complexation of monovalent sodium, potassium, rubidium, thallium and silver cations at 25° in aqueous solution has been carried out by ultrasonic absorption in the 15 to 205 MHz frequency range.

A concentration independent absorption with a maximum at 22.9 ± 0.5 MHz detected in aqueous solutions of 15-crown-5 with no cations added has been attributed to a conformational rearrangement of the crown ether. The kinetics of the complexation of the polyether with sodium, potassium, rubidium, silver and thallium(I) ions were then investigated at various polyether and metal concentrations with concentration dependent relaxations occurring between ~15 and ~55 MHz. These data, together with the conformational rearrangement data, were analyzed in terms of a two step mechanism:



in which CR₂ denotes the conformation of the ether which participates in the complexation reaction.

From kinetic considerations it is possible to calculate both k_{23} and k_{32} and to demonstrate that K_{21} is much less than unity.

Introduction

Macrocyclic polyethers are ever more widely used in chemistry as complexing agents of certain cations, and much work has been done on the fundamental properties of these compounds and their metal complexes.² The kinetics of the complexation process have also received some attention,³ mostly by nmr techniques.^{3b-e}

Infrared⁴, X-ray crystallographic⁵, and ab initio model studies⁶ indicate that the macrocyclic polyethers adopt different conformations in the complexed and uncomplexed states. This was pointed out in Chock's pioneering temperature jump kinetic study of metal complexation by dibenzo-30-crown-10 in methanol.^{3a} Previous studies in this laboratory⁷ of 18-crown-6 in water, by an ultrasonic absorption technique, confirmed the existence of a concentration independent relaxation ($f_R \approx 101$ MHz) in aqueous solutions of that particular pure crown ether that was attributed to a conformational equilibrium.

15-crown-5 has a similar geometry to 18-crown-6, although ring size and hole diameter of the former are smaller. The smaller ring size will cause 15-crown-5 to be more rigid and, as has been shown,⁸ complexation is less favored. These facts suggest that 15-crown-5 may undergo a slower conformational change than 18-crown-6, so much so that it might interfere with and slow down cation complexation. This possibility is considered below along with a comparison between the kinetics of cation complexation by 15-crown-5 and 18-crown-6. Finally, in aqueous 18-crown-6 complexation the enhanced stability of K^+ and Tl^+ complexes is attributable to their slower decomplexation rates. Since aqueous 15-crown-5 has no apparent cation selectivity

sequence,⁸ it is of interest to see whether the rates of decomplexation are also devoid of selectivity patterns.

Normal mode analysis^{9,10} of complex reactions provides a more complete understanding of the actual reactions being perturbed. In addition, it is possible to determine whether the reactions are coupled or not and to obtain relaxation times, amplitude factors, etc., for each so-called normal reaction. The troublesome question^{7,11} as to whether the conformational equilibrium constant $K_{21} \ll 1$ may also be answered through a normal mode analysis of the reaction scheme.

Experimental Section

Measurements of the ultrasonic absorption were carried out at a temperature of $25.0 \pm 0.1^\circ$ over the frequency range 15-205 MHz using a laser acousto-optic technique reported by this laboratory.¹² The argon ion laser was operated at the 514.5 nm green line, and the acoustic transducer was a gold plated 5MHz fundamental frequency, x-cut quartz crystal operated at odd harmonics over the frequency range. The acoustic beam was modulated under computer control to facilitate synchronous detection of the resulting optical signal, and adjustments in the ultrasonic transducer position, mirror position, and orientation of the sample cell plane to the Bragg angle were all computer controlled.

Solutions were prepared using deionized, redistilled water. The 15-crown-5 (Parish Chemical Company Provo, UT) was redistilled under vacuum (b.p. range collected $125 - 140^\circ$ at 0.5 mm Hg [$100-135^\circ$ at 0.2 mm Hg¹³]). Stock solutions were prepared by volume at 25° using a density of the pure product: 1.095 ± 0.001 g/ml.¹⁴ The inorganic ions were all of analytical reagent grade. Sodium, potassium and rubidium ions were added as chloride salts; thallium(I) and silver ions were in the form of nitrates.

Results

Total ultrasonic absorption data, expressed as $(\alpha/f^2)_T$ neper $\text{sec}^2 \text{cm}^{-1}$ for the pure 15-crown-5 aqueous solutions at different concentrations are presented in Table I and were analyzed in terms of relaxational and nonrelaxational contributions to the ultrasonic absorption¹⁵ using the following relation:

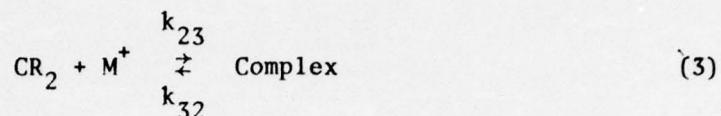
$$\alpha/f^2 = A [1 + (f/f_R)^2]^{-1} + B \quad (1)$$

wherein A is the relaxational amplitude of the process, f is the experimental frequency, f_R is the relaxational frequency of the sound absorbing process, and B is the solvent absorption. Table II shows these calculated parameters at different concentrations for the pure crown ether relaxation, resulting in a relaxation frequency of 22.9 MHz independent of concentration within an experimental error of ± 0.5 MHz. As would be expected from solutions of increased viscosity, the background absorption, B, at high frequencies was above that of pure water alone, ranging from an increase of 7×10^{-17} neper $\text{sec}^2 \text{cm}^{-1}$ over water for the most concentrated solution, 1 M, to 4×10^{-17} neper $\text{sec}^2 \text{cm}^{-1}$ over water for the 0.7 M concentration.

Similar ultrasonic absorption data for aqueous 15-crown-5 complexing with monovalent potassium, sodium, rubidium, thallium and silver cations are presented in Table III. In these cases only one relaxation process was detected. As in the pure 15-crown-5 case, and since relatively high concentration of electrolytes were used (up to 0.4 M), variable backgrounds were fitted to the data. The B values which always gave the best fit were from 21×10^{-17} to 21.7×10^{-17} neper $\text{sec}^2 \text{cm}^{-1}$, essentially that of pure water.¹⁶ Table IV shows the calculated relaxation parameters that give a best fit of the data in Table III.

Discussion

Denoting two different conformers of 15-crown-5 by CR_1 and CR_2 respectively the reaction scheme



suggested by Chock^{3a} for the case of cation complexation by dibenzo-30-crown-10 in methanol and also successfully used in the interpretation of cation complexation by 18-crown-6 in water^{7,11} can be fitted to the 15-crown-5 experimental data. However, in previous cases, the conformational relaxation, Eq. (2), was fast compared to that of the complexation step, Eq. (3). In the present case, relaxation frequencies for the two processes are quite close, which in itself does not allow any simplification of the kinetic expressions.

A normal mode analysis^{9,10} of the reaction scheme, Eqs. (2) and (3), yields an exact expression of the rate equation, reveals whether the two reactions are strongly, if at all, coupled, and also yields the normal reactions and their amplitude factors, Γ .

For the above reaction scheme the following secular determinant is obtained¹⁷

$$\begin{vmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{vmatrix} = \begin{vmatrix} k_{12} + k_{21} - \lambda & -k_{21} \\ -k_{23}[\text{M}^+] & k_{23}([\text{M}^+] + [\text{CR}_2]) + k_{32} - \lambda \end{vmatrix} = 0 \quad (4)$$

where the extent of coupling is determined by the magnitude of the terms $-k_{21}$ and $-k_{23}[\text{M}^+]$. Since reasonable estimates of k_{21} and k_{23} cannot be made, it is advantageous to examine the rigorous case of full coupling so that no assumptions regarding the relaxation times, rate constants, etc., are required. In such a case the result of Eq. (4) is the quadratic equation:

$$\tau^{-2} - S\tau^{-1} + P = 0 \quad (5)$$

where S and P are the sum and the product of the roots, given by the following expression:

$$S = k_{12} + k_{21} + k_{32} + k_{23} \left\{ \frac{1}{1 + K_{21}} ([CR_1] + [CR_2] + [M]^+) \right\} \quad (6)$$

$$P = k_{12} k_{23} ([CR_1] + [CR_2] + [M]^+) + k_{32} (k_{12} + k_{21}) \quad (7)$$

and in turn,

$$K_{21} = \frac{[CR_1]}{[CR_2]} = \frac{k_{21}}{k_{12}} \quad (8)$$

When only step I, Eq. (2), takes place, as in the pure 15-crown-5 experiments, the relaxation time for this process is given by:

$$\tau_p^{-1} = k_{12} + k_{21} \quad (9)$$

where the subscript p was chosen to denote pure crown. Substitution of this value and the related one: $k_{12} = \tau_p^{-1}/(1+K_{21})$, can be made into Eqs. (6) and (7). The result obtained

$$\tau^{-1} = k_{32} + k_{23} \left[\frac{([CR_1] + [CR_2])}{1 + K_{21}} + \left(\frac{\tau_p^{-1} - \frac{\tau_p^{-1}}{1+K_{21}}}{\tau^{-1} - \tau_p^{-1}} \right) [M]^+ \right] \quad (10)$$

can be arranged, for plotting purposes, as

$$\frac{\tau^{-1} - \tau_p^{-1}}{[M]^+} = k_{32} \left[\frac{(\tau^{-1} - \tau_p^{-1}) (1 + K_T ([CR_1] + [CR_2])) - \tau_p^{-1} [M]^+ K_T}{\tau^{-1} [M]^+} \right] + k_{23} \quad (11)$$

wherein:

$$K_T = \frac{[\text{Complex}]}{([CR_1] + [CR_2]) [M]^+} \quad (12)$$

denotes the experimental equilibrium constant for the overall complexation process. The equilibrium constants for the cation complexes of 15-crown-5 have been reported by Izatt *et al.*⁸ With their values both the equilibrium free crown and the equilibrium free metal concentrations can be calculated.

Eq. (11) gives a good fit of the experimental ultrasonic data (Fig. 1). The forward and reverse rate constants for metal ion complexation are the intercept and slope of the linear plot, respectively. The calculation of the second step equilibrium constant K_{23} , is given by:

$$K_{23} = \frac{[\text{Complex}]}{[\text{CR}_2][\text{M}^+]} = \frac{k_{23}}{k_{32}} \quad (13)$$

and K_{21} may be evaluated from:

$$1 + K_{21} = \frac{K_{23}}{K_T} \quad (14)$$

The results are shown in Table V. Unfortunately, in all cases, the calculated values of K_{23} lie within the error limits of the respective K_T values, therefore, K_{21} cannot be calculated with acceptable precision. In view of these results and heeding the error margins in the K_T values it is only possible to say that

$$K_{21} \leq 0.1$$

Using the maximum value for K_{21} and the associated rate constants in the eigenvalues of Eq. (4)

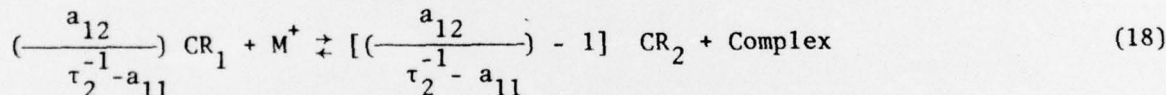
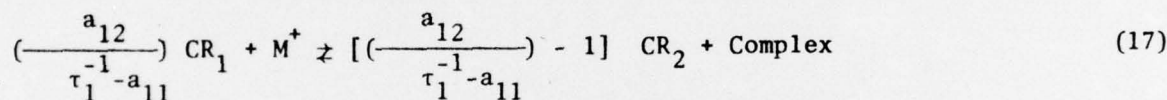
$$\frac{1}{\tau_1} = \lambda_1 = \frac{1}{2} [a_{11} + a_{22} + \sqrt{(a_{11} - a_{22})^2 + 4a_{12}a_{21}}] \quad (15)$$

$$\frac{1}{\tau_2} = \lambda_2 = \frac{1}{2} [a_{11} + a_{22} - \sqrt{(a_{11} - a_{22})^2 + 4a_{12}a_{21}}] \quad (16)$$

it can be determined whether $4a_{12}a_{21} \ll (a_{11} - a_{22})^2$, in which case coupling does not exist. For all cations in this study complexing with aqueous 15-crown-5 it was determined that $4a_{12}a_{21}$ was not negligible compared to $(a_{11} - a_{22})^2$, from which it may be concluded that the two reactions are coupled or are coupled, at least, in the case when K_{21} is at its maximum limit.

There still remains the possibility that K_{21} is far smaller than the upper limit 0.1 such that the reactions occur independent of each other since the conformational equilibrium is shifted largely toward the complexing form (i.e. the reactions exist uncoupled). There is no basis for assigning any specific value of 10^{-1} , 10^{-2} , 10^{-4} , etc. to K_{21} from the relaxation time information. The question thus arises: Will relaxation amplitudes yield a value of K_{21} ? We proceed now with the calculation of normal reactions, their amplitudes, etc. for the coupled and uncoupled situations.¹⁷

When the two equilibria, Eqs. (2) and (3), are coupled the normal reactions are



from which it follows that the amplitude factors, Γ_1 and Γ_2 , are ($\Gamma_n =$

$$\left[\sum_i \frac{\mu_{in}^2}{C_i} \right]^{-1})$$

$$\Gamma_1 = \left[\left(\frac{\frac{a_{12}}{\tau_1^{-1} - a_{11}}}{[CR_1]} \right)^2 + \frac{1}{[M^+]} + \left(\frac{\frac{a_{12}}{\tau_1^{-1} - a_{11}} - 1}{[CR_2]} \right)^2 + \frac{1}{[\text{Complex}]} \right]^{-1} \quad (19)$$

$$\Gamma_2 = \left[\left(\frac{\frac{a_{12}}{\tau_2^{-1} - a_{11}}}{[CR_1]} \right)^2 + \frac{1}{[M^+]} + \left(\frac{\frac{a_{12}}{\tau_2^{-1} - a_{11}} - 1}{[CR_2]} \right)^2 + \frac{1}{[\text{Complex}]} \right]^{-1} \quad (20)$$

Table VI is a listing of Γ_1 , Γ_2 , $f_{R,I}$, and $f_{R,II}$ for each of the cations at the investigated concentrations using a K_{21} of 0.1. In all cases the

amplitude factors, Γ_I and Γ_{II} , differ by less than one power of ten. The relaxation amplitudes, A_I and A_{II} , also shown in Table VI are calculated from the relation

$$A = \frac{2\pi^2 \rho v}{RT} [\Delta V_s^0 - \frac{\alpha_p}{\rho C_p} \Delta H^0]^2 \Gamma \tau \quad (21)$$

where ρ is the density, v the velocity (cm/s), R the gas constant (erg/deg mole), ΔV_s the volume change (cm³/mole), Γ the amplitude factor (mole/cm³), and τ the relaxation time and where the term in ΔH^0 is negligible. For Eq. (17) the volume change is ($\Delta V = \sum_n \mu_{1n} \bar{V}_{1n}$)

$$\Delta V_I = \left(\frac{a_{12}}{\tau_1^{-1} - a_{11}} \right) \Delta V_1^0 + \Delta V_2^0 \quad (22)$$

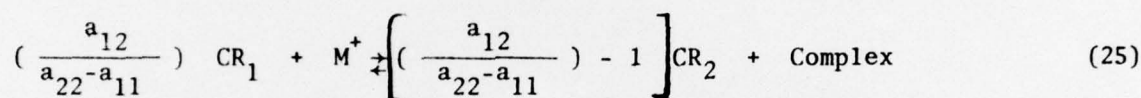
where ΔV_1^0 is the volume change for the step $CR_1 \rightleftharpoons CR_2$, and ΔV_2^0 is the volume change for the complexation step $CR_2 + M^+ \rightleftharpoons \text{Complex}$. Similarly the volume change for the second normal mode is

$$\Delta V_{II} = \left(\frac{a_{12}}{\tau_2^{-1} - a_{11}} \right) \Delta V_1^0 + \Delta V_2^0 \quad (23)$$

The values of ΔV_1^0 and ΔV_2^0 for 15-crown-5 are not known. However, the values of ΔV_1^0 and ΔV_2^0 for 18-crown-6 have been measured.¹⁸ Though the values of ΔV_1^0 and ΔV_2^0 may be expected to change some from 18-crown-6 to 15-crown-5 the 18-crown-6 values should be a satisfactory approximation for this study. Values of ΔV_I and ΔV_{II} are listed in Table VI along with the resulting values of A_I and A_{II} . A double relaxation should be observed with similar relaxation frequencies except for Rb^+ and Ag^+ . In these cases a single relaxation will be primarily observed corresponding to the first normal mode, Eq.(7). In all the complexation cases the relaxation frequencies ($\tau^{-1} = 2\pi f_R$) measured do not correspond to those predicted. Additionally, the calculated amplitudes are much larger than experimentally observed though this may be attributable to the approximate ΔV^0

values. Finally, it should be noted that in all cases the experimental relaxation curves were analyzed for double as well as a single relaxation with best fits being obtained for a single relaxation. When one assumes the two reactions, Eqs. (2) and (3), are coupled, theory predicts poorly what occurs experimentally.

The uncoupled case yields a better correspondence between theory and experiment. The normal reactions for the uncoupled case are:



with amplitude factors

$$\tau_1 = \left[\frac{1}{[CR_1]} + \frac{1}{[CR_2]} \right]^{-1} \quad (26)$$

$$\tau_2 = \left[\left(\frac{a_{12}}{a_{22}-a_{11}} \right)^2 \frac{1}{[CR_1]} + \frac{1}{[M^+]} + \left(\frac{a_{12}}{a_{22}-a_{11}} - 1 \right)^2 \frac{1}{[CR_2]} + \frac{1}{[\text{Complex}]} \right]^{-1} \quad (27)$$

The relaxation times for the two normal reactions when uncoupled are

$$\tau_1^{-1} = k_{12} + k_{21} \quad (28)$$

and

$$\tau_2^{-1} = k_{23} ([CR_2] + [M^+]) + k_{32} \quad (29)$$

or its equivalent

$$\tau_2^{-1} = k_{23} ([CR_1] + [CR_2] + [M^+] + K_T^{-1}) \quad (30)$$

Note that expression (29) is different from the reciprocal relaxation time

$$\tau_2^{-1} = \frac{k_{23}}{1+K_{21}} ([CR_1] + [CR_2] + [M^+]) + k_{32} \text{ for 18-crown-6 complexation.}^{7,11}$$

Table VII lists the complexation and decomplexation rate constants assuming the two reactions, Eqs. (2) and (3), are uncoupled. Figure 2 is a plot of Eq. (30) for the various complexes studied. Note that only for Ag^+ and Tl^+ do the values of k_{23} and k_{32} change in going from the coupled to uncoupled case.

Table VIII is a listing of Γ_1 , Γ_2 , $f_{R,I}$ and $f_{R,II}$ for each of the cations at the investigated concentrations assuming $K_{21} = 10^{-3}$, a value small enough to assure that Eqs. (2) and (3) are uncoupled. Table VIII clearly shows that the second normal reaction (25) has a much larger amplitude factor (Γ_2). In the uncoupled case the amplitudes are given by

$$A_{I,II} = \frac{2\pi^2 \rho v}{RT} (\Delta V_s)_{I,II}^2 \Gamma_{I,II} \tau_{I,II} \quad (31)$$

where the value of ΔV_I and ΔV_{II} are again from the 18-crown-6 case¹⁸ as listed in Table VI.

Clearly, the conformational rearrangement should be unobservable while the complexation step has a much larger, observable amplitude. In addition, the reciprocal relaxation time ($\tau^{-1} = 2\pi f_R$) for the second normal reaction closely approximates experiment. Thus in the uncoupled case ($K_{21} < 10^{-2}$) there is much better agreement between theory and experiment than in the coupled case. Since the reactions are uncoupled, the relaxation time of the conformational rearrangement of 15-crown-5, Eq. (2), does not affect the rate of complexation. This does not preclude, however, the possibility that a conformational rearrangement during complexation could be rate-limiting. This is, therefore, a very interesting case since even though the two reactions, Eqs. (2) and (3), occur at similar rates the fact that $K_{21} < 10^{-2}$ results in the two reactions occurring independent of one another.

Inspection of Table VII reveals that the rates of complexation for Na^+ , K^+ and Rb^+ are essentially the same as for their complexation with aqueous 18-crown-6 [2.2 , 4.3 and $4.4 \times 10^8 \text{ M}^{-1} \text{ sec}^{-1}$ respectively].¹¹ This suggests that the mechanism for aqueous 15-crown-5 and aqueous 18-crown-6 complexing these cations is the same. Rb^+ loses water of solvation slightly faster than K^+ [3×10^9 and $1 \times 10^9 \text{ sec}^{-1}$ respectively].¹⁹ Since for aqueous 15-crown-5 the complexation of K^+ and Rb^+ are the same as in aqueous 18-crown-6, it is possible that water loss

is not rate-determining but rather that there is a new rate-limiting step (when water loss is faster than that for K^+) such as a conformational rearrangement of the ligand during complexation, i.e. $CR_2 \rightleftharpoons CR_2'$. It is also possible that for the alkali metal cations with a radius larger than K^+ the water loss rate remains essentially constant.¹¹

For 15-crown-5 complexation of Ag^+ the specific rate is quite different than that for 18-crown-6 complexation of Ag^+ [$11.2 \times 10^8 M^{-1} sec^{-1}$].¹¹ In fact, 15-crown-5 complexes silver at a slower rate than it does thallium(I). Evidently, the mechanism by which Ag^+ is complexed by aqueous 18-crown-6 is not the same as its complexation by aqueous 15-crown-5. It is difficult to ascertain by what mechanism Tl^+ and Ag^+ are complexed by 15-crown-5. Since Ag^+ has a smaller ionic radius than Tl^+ , water loss could be rate-determining for Ag^+ .¹⁹ An alternative explanation for why 15-crown-5 complexes Ag^+ more slowly than does 18-crown-6 is that Ag^+ has a linear bonding geometry²⁰ and therefore cannot bond as effectively the non-symmetrical (i.e. pentagonal arrangement of oxygen atoms) characterizing the relatively rigid 15-crown-5 as it can the symmetrical 18-crown-6 (i.e. hexagonal arrangement of oxygen atoms). To prove this point it would be necessary to investigate the kinetics of Ag^+ complexation by 12-crown-4 and possibly 21-crown-7.

The stability constants for the aqueous 15-crown-5 complexes of K^+ , Rb^+ , Na^+ , Ag^+ , and Tl^+ are much lower than for the similar aqueous 18-crown-6 complexes, and, in addition, there is no actual selectivity pattern for 15-crown-5 in contrast to 18-crown-6.⁸ Liesegang *et al.*^{7,11} observed that for aqueous 18-crown-6 the stability constants were primarily affected by the decomplexation rates. This fact is further borne out by 15-crown-5 since the decomplexation rates are all within an order of magnitude of one another thus causing no apparent differences in the stability constants as observed thermodynamically. In addition,

the smaller stability constants for 15-crown-5 compared to 18-crown-6 are attributable to the faster decomplexation rate of the 15-crown-5 complexes.

Acknowledgement

This work was sponsored by a contract from the Office of Naval Research and by Grant No. AFOSR 73-2444C from the Directorate of Chemical Sciences, Air Force Office of Scientific Research.

References and Notes

1. (a) On leave from the University of Salamanca, Spain;
(b) University of Utah; (c) University of Idaho; (d) Oklahoma State University.
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Table I. EXPERIMENTAL ABSORPTION AS (α/f^2) IN $\text{Np cm}^{-1}\text{sec}^2$
FOR AQUEOUS 15-CROWN-5 AT 25°

[15-crown-5] = 1.00 M		[15-crown-5] = 0.801 M		[15-crown-5] = 0.714 M	
$10^{17} (\alpha/f^2)_{\text{exptl.}}$		$10^{17} (\alpha/f^2)_{\text{exptl.}}$		$10^{17} (\alpha/f^2)_{\text{exptl.}}$	
$\text{Np cm}^{-1}\text{sec}^2$	f, MHz	$\text{Np cm}^{-1}\text{sec}^2$	f, MHz	$\text{Np cm}^{-1}\text{sec}^2$	f, MHz
40.94	15.18	36.17	15.11	33.95	15.20
35.16	25.26	32.62	25.29	30.87	25.30
32.94	35.42	30.47	35.41	29.48	35.37
31.88	45.56	29.36	45.60	28.30	45.58
30.71	55.70	28.28	55.72	27.78	55.70
30.66	65.82	27.86	65.83	27.39	65.82
29.94	75.94	27.68	75.94	27.27	75.93
29.67	86.08	27.52	86.06	26.90	86.08
29.48	96.18	26.90	96.20	26.90	96.19
29.12	106.3	26.86	106.3	26.40	106.3
28.87	116.4	26.97	116.4	26.12	116.4
28.57	126.5	27.12	126.6	25.82	126.6
28.72	136.7	26.83	136.7	26.08	136.7
28.52	146.8	26.34	146.7	26.21	146.8
28.24	156.9	25.68	156.9	26.04	156.9
28.13	167.1	25.41	167.1	26.90	167.1
28.17	177.2	25.65	177.2	24.79	177.2
28.21	187.3	25.84	187.3	25.00	187.3
27.92	197.4	26.17	197.5	25.47	197.4
28.03	207.6			23.43	207.6
26.51	217.7				
26.16	227.8				
27.04	238.0				

TABLE II. RELAXATION PARAMETERS FROM COMPUTER ANALYSIS
FOR AQUEOUS 15-CROWN-5 AT 25°^a

<u>[15-Crown-5], M</u>	<u>f_{r,I}, MHz</u>	$10^{17} A$	$10^{17} A$	10^{18}R.M.S.^b
		<u>Np cm⁻¹ sec²</u>	<u>Np cm⁻¹ sec²</u>	
1.00	23.11	16.28	28.25	1.0
0.801	22.52	14.81	26.31	0.7
0.714	23.11	11.94	25.81	1.0

f_{r,I} average = 22.91 MHz ± 0.4 MHz.

^aAll symbols as defined in text.

^bRoot-mean-square deviation.

Table IIIa. EXPERIMENTAL ULTRASONIC ABSORPTION DATA AS (α/f^2)

FOR AQUEOUS KCl AND 15-CROWN-5 AT 25°

$[K^+]_0 = 0.100 \text{ M}$ $[15\text{-Crown-5}]_0 = 0.100 \text{ M}$		$[K^+]_0 = 0.200 \text{ M}$ $[15\text{-Crown-5}]_0 = 0.100 \text{ M}$		$[K^+]_0 = 0.306 \text{ M}$ $[15\text{-Crown-5}]_0 = 0.100 \text{ M}$		$[K^+]_0 = 0.404 \text{ M}$ $[15\text{-Crown-5}]_0 = 0.100 \text{ M}$	
$10^{17}(\alpha/f^2)_{\text{exptl.}}$ $\text{Np cm}^{-1} \text{sec}^2$	f, MHz	$10^{17}(\alpha/f^2)_{\text{exptl.}}$ $\text{Np cm}^{-1} \text{sec}^2$	f, MHz	$10^{17}(\alpha/f^2)_{\text{exptl.}}$ $\text{Np cm}^{-1} \text{sec}^2$	f, MHz	$10^{17}(\alpha/f^2)_{\text{exptl.}}$ $\text{Np cm}^{-1} \text{sec}^2$	f, MHz
72.23	15.16	82.76	15.00	77.78	15.19	68.77	15.20
55.19	25.30	62.27	25.31	60.36	25.31	59.81	25.29
43.54	35.39	49.27	35.43	50.99	35.44	51.81	35.42
36.38	45.60	41.55	45.61	44.02	45.58	43.63	45.56
32.58	55.70	36.73	55.70	38.67	55.68	38.96	55.69
29.18	65.77	32.81	65.82	35.04	65.81	35.15	65.81
27.56	75.93	30.41	75.93	32.53	75.95	32.53	75.93
26.21	86.06	28.78	86.05	30.31	86.06	30.51	86.06
25.29	96.18	27.15	96.18	28.41	96.18	28.64	96.19
24.71	106.4	25.92	106.3	26.92	106.3	27.60	106.3
24.01	106.4	25.27	116.4	26.33	116.4	25.46	116.4
23.14	126.6	24.37	126.6	25.38	126.6	25.48	126.5
23.15	136.7	24.01	136.7	24.97	136.7	24.95	136.7
22.63	146.7	23.14	146.8	23.70	146.8	24.26	146.8
22.49	156.9	23.41	156.9	23.32	156.9	23.66	156.9
22.10	167.1	21.43	167.0	22.45	167.1	23.48	167.1
21.93	177.2	19.94	177.2	21.72	177.2	23.05	177.2
21.38	187.3	21.30	187.3	23.44	187.3	22.73	187.3
20.99	197.4			21.96	197.4	22.47	197.5
				22.21	207.6	22.23	207.6
				22.09	217.7	21.87	217.7
						22.57	227.8

^a Subscript zero on bracketed concentrations denotes total concentration in all species in this and subsequent tables.

Table IIIb. EXPERIMENTAL ULTRASONIC ABSORPTION DATA

AS (α/f^2) FOR AQUEOUS TiNO_3 AND 15-CROWN-5 AT 25°

$[\text{Ti}^+]_0 = 0.137 \text{ M}$ $[\text{15-Crown-5}]_0 = 0.120 \text{ M}$		$[\text{Ti}^+]_0 = 0.170 \text{ M}$ $[\text{15-Crown-5}]_0 = 0.120 \text{ M}$		$[\text{Ti}^+]_0 = 0.263 \text{ M}$ $[\text{15-Crown-5}]_0 = 0.120 \text{ M}$		$[\text{Ti}^+]_0 = 0.320 \text{ M}$ $[\text{15-Crown-5}]_0 = 0.120 \text{ M}$	
$10^{17}(\alpha/f^2)_{\text{exptl.}}$	f, MHz	$10^{17}(\alpha/f^2)_{\text{exptl.}}$	f, MHz	$10^{17}(\alpha/f^2)_{\text{exptl.}}$	f, MHz	$10^{17}(\alpha/f^2)_{\text{exptl.}}$	f, MHz
Np cm ⁻¹ sec ²		Np cm ⁻¹ sec ²		Np cm ⁻¹ sec ²		Np cm ⁻¹ sec ²	
162.0	15.18	151.7	15.19	90.28	15.16	89.86	15.18
107.6	25.30	107.1	25.30	74.80	25.28	75.51	25.32
76.38	35.41	78.04	35.43	58.93	35.43	62.03	35.42
58.33	45.59	62.21	45.57	48.91	45.57	52.81	45.56
48.37	55.72	49.80	55.70	42.16	55.71	45.38	55.67
41.28	65.81	41.63	65.82	37.22	65.83	40.00	65.82
36.77	75.93	36.60	75.94	33.95	75.95	36.60	75.92
33.46	86.06	33.80	86.06	31.57	86.06	33.75	86.06
31.34	96.19	31.45	96.19	30.20	96.19	32.16	96.19
29.43	106.3	29.60	106.3	28.02	106.3	29.75	106.3
28.13	116.4	27.99	116.4	26.69	116.4	28.38	116.4
26.69	126.5	27.01	126.6	25.70	126.5	27.50	126.6
26.16	136.7	26.56	136.7	24.95	136.7	27.01	136.7
25.02	146.8	25.60	146.8	24.68	146.8	26.15	146.8
24.90	156.9	24.51	156.9	24.46	156.9	25.33	156.9
24.55	167.0	23.04	167.1	22.37	167.0	24.31	167.1
24.36	177.2	22.16	177.2	21.94	177.2	23.51	177.2
23.95	187.3	21.71	187.3	21.19	187.3		
23.28	197.4	20.84	197.4				

Table IIIc. EXPERIMENTAL ABSORPTION AS (α/f^2) IN $\text{Np cm}^{-1}\text{sec}^2$ FOR
AQUEOUS SODIUM CHLORIDE AND 15-CROWN-5 AT 25°^a

[NaCl] ₀ = 0.217 F [15-Crown-5] ₀ = 0.0953 M		[NaCl] ₀ = 0.327 F [15-Crown-5] ₀ = 0.0905 M		[NaCl] ₀ = 0.417 F [15-Crown-5] ₀ = 0.0906 M	
$10^{17} \{ \alpha/f^2 \}$ exptl., <u>$\text{Np cm}^{-1}\text{sec}^2$</u>	<u>f, MHz</u>	$10^{17} \{ \alpha/f^2 \}$ exptl., <u>$\text{Np cm}^{-1}\text{sec}^2$</u>	<u>f, MHz</u>	$10^{17} \{ \alpha/f \}$ exptl., <u>$\text{Np cm}^{-1}\text{sec}^2$</u>	<u>f, MHz</u>
180.5	15.04	176.7	15.05	172.2	15.05
111.8	25.08	112.6	25.09	117.1	25.09
76.79	35.14	80.85	35.12	85.03	35.14
56.73	45.19	60.93	45.23	64.39	45.23
45.34	55.24	49.08	55.26	51.90	55.26
39.27	65.29	41.92	65.29	44.22	65.34
34.98	75.33	38.62	75.33	38.99	75.37
32.16	85.39	34.63	85.36	35.22	85.42
29.87	95.41	30.64	95.40	32.85	95.44
28.33	105.5	29.75	105.4	30.67	105.5
27.05	115.5	28.10	115.5	29.18	115.5
26.23	125.5	27.22	125.5	27.80	125.6
25.30	135.6	26.11	135.6	26.87	135.5
24.72	145.6	26.01	145.6	25.96	145.7
23.52	155.7	23.69	155.7	25.50	155.7
23.67	165.7	22.93	165.7	24.41	165.8
23.24	175.8	22.90	175.8	23.08	176.8
23.10	185.8	23.75	185.8		
22.60	195.9	21.80	195.8		
21.58	205.9				

Table IIIId. EXPERIMENTAL ABSORPTION AS (α/f^2) IN $\text{Np cm}^{-1}\text{sec}^2$

FOR AQUEOUS RUBIDIUM CHLORIDE AND 15-CROWN-5 AT 25°

[illegible]

Table IIIe. EXPERIMENTAL ABSORPTION AS (α/f^2) IN $\text{Np cm}^{-1}\text{sec}^2$

FOR AQUEOUS SILVER NITRATE AND 15-CROWN-5 AT 25°

$[\text{AgNO}_3]_0 = 0.115 \text{ F}$ $[\text{15-Crown-5}]_0 = 0.117 \text{ M}$		$[\text{AgNO}_3]_0 = 0.215 \text{ F}$ $[\text{15-Crown-5}]_0 = 0.117 \text{ M}$		$[\text{AgNO}_3]_0 = 0.359 \text{ F}$ $[\text{15-Crown-5}]_0 = 0.117 \text{ M}$		$[\text{AgNO}_3]_0 = 0.443 \text{ F}$ $[\text{15-Crown-5}]_0 = 0.105 \text{ M}$	
$10^{17}\{\alpha/f^2\}$ exptl., $\text{Np cm}^{-1}\text{sec}^2$		$10^{17}\{\alpha/f^2\}$ exptl., $\text{Np cm}^{-1}\text{sec}^2$		$10^{17}\{\alpha/f^2\}$ exptl., $\text{Np cm}^{-1}\text{sec}^2$		$10^{17}\{\alpha/f^2\}$ exptl., $\text{Np cm}^{-1}\text{sec}^2$	
f, MHz		f, MHz		f, MHz		f, MHz	
155.2	15.05	147.3	15.10	86.69	25.11	71.36	25.12
112.5	25.09	114.3	25.07	72.21	35.15	58.55	35.14
81.90	35.13	90.19	35.15	62.56	45.21	52.60	45.20
62.80	45.21	72.79	45.21	54.87	55.26	47.36	55.25
51.57	55.29	60.62	55.26	48.71	65.30	42.75	65.30
44.60	65.31	52.11	65.30	43.47	75.35	40.13	75.35
39.29	75.36	45.23	75.34	39.76	85.40	37.26	85.40
36.07	85.37	40.21	85.40	36.72	95.42	35.18	95.45
32.89	95.41	37.02	95.41	34.32	105.5	32.62	105.5
30.19	105.5	34.35	105.5	31.50	115.5	31.28	115.5
28.56	115.5	31.62	115.5	29.28	125.6	29.17	125.6
28.02	125.6	30.30	125.6	29.04	135.6	28.78	135.6
26.16	135.6	23.69	185.8	26.06	155.7	27.50	145.7
26.03	145.7	25.30	195.9	25.33	165.7	26.19	175.8
25.25	155.7	25.30	205.9	25.24	195.9	26.06	185.8
25.48	165.8						
24.65	175.8						

Table IV. RELAXATION PARAMETERS FROM COMPUTER ANALYSIS

$[\text{NaCl}]_{\text{O},\text{M}}$	$[\text{15-Crown-5}]_{\text{O},\text{M}}$	$f_{\text{T,II}} \text{ MHz}$	10^{17} A	10^{18} R.M.S.
0.217	0.0953	16.99	284.	1.6
0.327	0.0905	19.64	244.	1.5
0.417	0.0906	21.95	224.	0.9
$[\text{KCl}]_{\text{O},\text{M}}$	$[\text{15-Crown-5}]_{\text{O},\text{M}}$	$f_{\text{T,II}} \text{ MHz}$	10^{17} A	10^{18} R.M.S.
0.100	0.100	21.86	77.4	1.4
0.200	0.100	25.73	82.1	1.1
0.306	0.100	32.11	68.2	1.0
0.404	0.100	38.40	55.6	0.9
$[\text{RbCl}]_{\text{O},\text{M}}$	$[\text{15-Crown-5}]_{\text{O},\text{M}}$	$f_{\text{T,II}} \text{ MHz}$	10^{17} A	10^{18} R.M.S.
0.0959	0.117	31.11	39.6	0.7
0.180	0.117	35.20	51.6	0.7
0.278	0.117	37.58	50.5	2.4
0.466	0.117	44.28	43.5	0.8
$[\text{AgNO}_3]_{\text{O},\text{M}}$	$[\text{15-Crown-5}]_{\text{O},\text{M}}$	$f_{\text{T,II}} \text{ MHz}$	10^{17} A	10^{18} R.M.S.
0.115	0.117	24.40	184.	1.2
0.215	0.117	31.82	154.	1.6
0.359	0.117	43.74	85.5	1.1
0.443	0.105	55.68	51.5	0.5
$[\text{TlNO}_3]_{\text{O},\text{M}}$	$[\text{15-Crown-5}]_{\text{O},\text{M}}$	$f_{\text{T,II}} \text{ MHz}$	10^{17} A	10^{18} R.M.S.
0.137	0.120	20.22	222	0.9
0.170	0.120	23.53	184.	1.9
0.263	0.0900	31.10	85.9	1.4
0.320	0.102	35.44	81.3	0.9

Table V. RATE CONSTANTS AND EQUILIBRIUM CONSTANT FOR COMPLEXATION
BY 15-CROWN-5 IN AQUEOUS SOLUTION AT 25° WHEN COUPLING
IS ASSUMED^a

Cation	$k_{23}, M^{-1}sec^{-1}$	k_{32}, sec^{-1}	$\log K_{23}(calc.)$	$\log K_T^b$
Na ⁺	$2.6 \cdot 10^8$	$5.1 \cdot 10^7$	0.71	0.70 ± 0.04
K ⁺	$4.3 \cdot 10^8$	$7.8 \cdot 10^7$	0.74	0.74 ± 0.04
Rb ⁺	$4.4 \cdot 10^8$	$1.4 \cdot 10^8$	0.50	0.6 ± 0.1
Tl ⁺	$8.0 \cdot 10^8$	$5.0 \cdot 10^7$	1.20	1.23 ± 0.04
Ag ⁺	$6.7 \cdot 10^8$	$8.2 \cdot 10^7$	0.91	0.94 ± 0.04

^a For this and subsequent tables see text for definition of coupling and uncoupling cases.

^b Ref. 8.

TABLE VI. Relaxation frequencies, amplitude factors, amplitudes^a and volume changes for the normal reactions when $k_{21} = 0.1$ (coupled case) ($k_{12} = 1.3 \times 10^8 \text{ sec}^{-1}$; $k_{21} = 1.3 \times 10^7 \text{ sec}^{-1}$)

SODIUM ($k_{23} = 2.6 \times 10^8$; $k_{32} = 5.1 \times 10^7$)									
$[M^+]_i F [15\text{-Crown-5}]_i^M$	$f_{R,I}$ MHz	$f_{R,II}$ MHz	Γ_I mol/ml.	Γ_{II} mol/ml.	$A_I 10^{17}$ Np cm ⁻¹ sec ²	$A_{II} 10^{17}$ Np cm ⁻¹ sec ²	ΔV_I cm ³ /mol	ΔV_{II} cm ³ /mol	
0.217	0.0953	15.3	2.73×10^{-6}	1.80×10^{-5}	97.3	134.5	-22.0	-8.21	
0.327	0.0905	16.9	5.87×10^{-6}	1.44×10^{-5}	106.3	79.0	-16.4	-7.44	
0.417	0.0906	18.0	8.49×10^{-6}	1.10×10^{-5}	107.9	44.9	-14.4	-6.68	
POTASSIUM ($k_{23} = 4.3 \times 10^8$; $k_{32} = 7.8 \times 10^7$)									
0.100	0.100	19.6	8.88×10^{-6}	5.44×10^{-6}	231.7	11.9	-19.8	-5.53	
0.200	0.100	20.4	7.19×10^{-6}	1.60×10^{-5}	184.4	171.7	-20.9	-11.5	
0.306	0.100	20.9	4.99×10^{-6}	2.10×10^{-5}	119.5	298.3	-21.8	-13.3	
0.404	0.100	20.4	1.61×10^{-5}	5.00×10^{-6}	185.1	20.5	-16.4	-7.41	
RUBIDIUM ($k_{23} = 4.4 \times 10^8$; $k_{32} = 1.4 \times 10^8$)									
0.0950	0.117	22.0	1.38×10^{-5}	1.47×10^{-6}	108.6	22.9	-12.2	+13.0	
0.180	0.117	21.6	1.92×10^{-5}	2.50×10^{-6}	120.4	8.42	-11.6	+5.80	
0.278	0.117	21.3	2.27×10^{-5}	3.04×10^{-6}	116.8	3.73	-11.2	+3.32	
0.466	0.117	21.2	2.20×10^{-5}	2.97×10^{-6}	85.2	1.13	-10.9	+1.67	
SILVER ($k_{23} = 6.7 \times 10^8$; $k_{32} = 8.2 \times 10^7$)									
0.115	0.117	20.7	1.31×10^{-5}	6.11×10^{-6}	143.3	0.15	-13.7	-1.16	
0.215	0.117	20.5	1.79×10^{-5}	5.66×10^{-6}	125.8	0.80	-12.2	-1.88	
0.359	0.117	20.5	1.81×10^{-5}	3.95×10^{-6}	82.9	0.42	-11.4	-1.72	
0.443	0.105	20.5	1.51×10^{-5}	2.87×10^{-6}	56.7	0.24	-11.2	-1.60	
THALLIUM(I) ($k_{23} = 8.0 \times 10^8$; $k_{32} = 5.0 \times 10^7$)									
0.137	0.120	18.8	8.83×10^{-6}	1.17×10^{-5}	244.9	121.3	-20.8	-10.9	
0.170	0.120	19.1	1.10×10^{-5}	1.02×10^{-5}	248.1	97.9	-19.4	-10.6	
0.263	0.0900	19.6	1.04×10^{-5}	4.32×10^{-6}	144.4	33.0	-17.5	-9.65	
0.320	0.102	19.9	1.14×10^{-5}	3.60×10^{-6}	132.6	23.5	-17.1	-9.04	

^a Amplitude is defined as $A_i = \frac{2\pi\nu}{RT} (\Delta V^\circ - \frac{\alpha\rho}{\rho C_p} \Delta H^\circ)^2 \Gamma_i \tau_i$, where the ΔV° used are those for 18-crown-6 complexation of the same cations, and conformational equilibrium.

Table VII. RATE CONSTANTS FOR COMPLEXATION BY 15-CROWN-5
IN AQUEOUS SOLUTION AT 25° WHEN UNCOUPLING IS ASSUMED

<u>Cation</u>	<u>$k_{23}, M^{-1}sec^{-1}$</u>	<u>k_{32}, sec^{-1}</u>
Na ⁺	2.4×10^8	4.8×10^7
K ⁺	4.3×10^8	7.8×10^7
Rb ⁺	4.6×10^8	1.2×10^8
Tl ⁺	7.1×10^8	4.2×10^8
Ag ⁺	6.4×10^8	7.4×10^8

TABLE VIII. Relaxation frequencies, amplitude factors and amplitudes^a for the normal Reaction modes with $K_{21} = 10^{-3}$ (uncoupled case) ($k_{12} = 1.44 \times 10^8$; $k_{21} = 1.44 \times 10^5$)

SODIUM ($k_{23} = 2.4 \times 10^8$; $k_{32} = 4.8 \cdot 10^7$)							
$[M^+]_F$	$[15\text{-Crown-5}]_M$	$f_{R,I}$ MHz	$f_{R,II}$ MHz	Γ_I mol./ml.	Γ_{II} mol./ml.	$A_I 10^{17}$ Np cm ⁻¹ sec ²	$A_{II} 10^{17}$ Np cm ⁻¹ sec ²
0.217	0.0953	22.9	16.2	5.09×10^{-8}	2.07×10^{-5}	0.49	269.5
0.327	0.0905	22.9	19.6	3.80×10^{-8}	1.97×10^{-5}	0.37	213.0
0.417	0.0906	22.9	22.6	3.24×10^{-8}	4.64×10^{-6}	0.31	40.6
POTASSIUM ($k_{23} = 4.3 \times 10^8$; $k_{32} = 4.8 \cdot 10^7$)							
0.100	0.100	22.9	22.3	7.16×10^{-8}	1.21×10^{-5}	0.74	215.1
0.200	0.100	22.9	26.6	5.40×10^{-8}	2.12×10^{-5}	0.56	315.9
0.306	0.100	22.9	32.3	4.23×10^{-8}	2.22×10^{-5}	0.44	272.1
0.404	0.100	22.9	38.0	3.49×10^{-8}	2.13×10^{-5}	0.36	221.8
RUBIDIUM ($k_{23} = 4.6 \times 10^8$; $k_{32} = 11.6 \times 10^7$)							
0.0950	0.117	22.9	30.2	9.15×10^{-8}	1.55×10^{-5}	0.87	94.4
0.180	0.117	22.9	34.4	7.44×10^{-8}	2.28×10^{-5}	0.71	122.1
0.278	0.117	22.9	39.3	6.19×10^{-8}	2.58×10^{-5}	0.59	120.9
0.466	0.117	22.9	50.8	4.55×10^{-8}	2.60×10^{-5}	0.43	94.3
SILVER ($k_{23} = 6.4 \times 10^8$; $k_{32} = 7.4 \times 10^7$)							
0.115	0.117	22.9	26.4	7.24×10^{-8}	1.97×10^{-5}	0.75	141.1
0.215	0.117	22.9	32.1	5.08×10^{-8}	2.41×10^{-5}	0.52	141.9
0.359	0.117	22.9	43.4	3.43×10^{-8}	2.23×10^{-5}	0.35	97.1
0.443	0.105	22.9	51.2	2.52×10^{-8}	1.82×10^{-5}	0.26	67.2
THALLIUM ($k_{23} = 7.1 \times 10^8$; $k_{32} = 4.7 \times 10^7$)							
0.137	0.120	22.9	21.6	5.42×10^{-8}	1.84×10^{-5}	0.56	380.0
0.170	0.120	22.9	23.4	4.57×10^{-8}	1.06×10^{-5}	0.47	202.5
0.263	0.0900	22.9	31.7	2.09×10^{-8}	1.48×10^{-5}	0.21	208.9
0.320	0.102	22.9	26.6	2.02×10^{-8}	1.52×10^{-5}	0.21	185.6

^a Amplitude A is defined as $A = \frac{2\pi \rho V}{RT} (\Delta V^\circ - \frac{\partial \rho}{\partial C} \Delta H^\circ)^2 \Gamma \tau$ where the ΔV° used are those for 18-crown-6 complexation of the same cation, and conformational equilibrium.

FIGURE CAPTIONS

Fig. 1. Plot of the silver, thallium and potassium ultrasonic absorption data of Table IV in terms of Eq. (11). Data for sodium and rubidium have not been included for clarity.

Fig. 2. Plot of all the ultrasonic absorption data of Table IV in terms of Eq. (30).

